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Brondijk, J. J.; Li, X.; Akkerman, H. B.; Blom, P. W. M.; de Boer, B.

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# Microcontact printing of self-assembled monolayers to pattern the light-emission of polymeric light-emitting diodes

**J.J. Brondijk · X. Li · H.B. Akkerman · P.W.M. Blom · B. de Boer**

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**Abstract** By patterning a self-assembled monolayer (SAM) of thiolated molecules with opposing dipole moments on a gold anode of a polymer light-emitting diode (PLED), the charge injection and, therefore, the light-emission of the device can be controlled with a micrometer-scale resolution. Gold surfaces were modified with SAMs based on alkanethiols and perfluorinated alkanethiols, applied by microcontact printing, and their work functions have been measured. The molecules form a chemisorbed monolayer of only ∼1.5 nm on the gold surface, thereby locally changing the work function of the metal. Kelvin probe measurements show that the local work function can be tuned from 4.3 to 5.5 eV, which implies that this anode can be used as a hole blocking electrode or as a hole injecting electrode, respectively, in PLEDs based on poly(*p*-phenylene vinylene) (PPV) derivatives. By microcontact printing of SAMs with opposing dipole moments, the work function was locally modified and the charge injection in the PLED could be controlled down to the micrometer length scale. Consequently, the local light-emission exhibits a high contrast. Microcontact printing of SAMs is a simple and inexpensive method to pattern, with micrometer resolution, the light-emission for low-end applications like static displays.

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Both authors (J.J. Brondijk and X. Li) contributed equally.

J.J. Brondijk · X. Li · H.B. Akkerman · P.W.M. Blom · B. de Boer (✉)
Molecular Electronics, Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG, Groningen, The Netherlands
e-mail: b.de.boer@rug.nl
Fax: +31-50-3638751

## 1 Introduction

Over the last decades, research efforts in the field of organic electronics have significantly been motivated by the promising properties of organic materials for use in devices which are low-cost and easily manufactured for low-end applications. Examples of such applications include displays [1], disposable sensors [2, 3] and RFID-tags [4–6]. Since it is highly cost-effective to use techniques which are compatible with conventional high-throughput printing procedures, the use of flexible device substrates, and patterning techniques capable of handling such substrates, received much interest [7]. Among various patterning methods, including ink-jet printing [8–10], laser ablation [11, 12] and various other techniques [13–17], soft lithography is one of the most widely studied techniques [18, 19].

Independently of the manufacturing techniques used for organic electronic devices, charge injection is recognized as one of the major processes determining the performance of the device. Charge injection from a metal contact into an organic semiconductor is primarily determined by the energy difference between the metal work function and the highest occupied molecular orbital (HOMO) for hole injection, or the energy difference between the metal work function and the lowest unoccupied molecular orbital (LUMO) for electron injection. Therefore, controlling and tuning the metal work function is of high importance, which was demonstrated previously for several metals by simply applying a self-assembled monolayer (SAM) to the metal surfaces [20, 21].

By the absorption of a self-assembled monolayer (SAM), the effective work function of Au can be increased by 0.9 eV or decreased by 0.45 eV [20–22]. Similar work function changes have been reported for silver electrodes covered

with a SAM. This implies that, when interfaced with an organic conjugated polymer with a suitable HOMO, the contact can be tuned from a blocking contact to an Ohmic contact. Organic devices with SAM-modified copper [21] or silver [20] contacts show orders of magnitude difference in current, depending on the dipole moment of the molecules used for the monolayer. Without taking into account the Au-S bond induced dipole moment, the work function shifts of SAM-modified gold can be estimated to be $-1.0$ eV for 1-decanethiol (DT) and $+1.3$ eV for $1H,1H,2H,2H$-perfluorodecanethiol (PFDT) [20]. The work function shift is expected to be smaller for areas with a SAM applied by microcontact printing, due to the formation of a SAM with more defects, and thereby a lower grafting density.

Apart from the effect of changing the effective work function of the electrode, a SAM is a high-bandgap material and therefore adds a very thin insulating layer to the electrode. This may increase the contact resistance of the metal–semiconductor interface, which can lower the device current. However, in our devices this effect is small compared to the effect of a shifted work function [23, 24]. Here, we apply a single monolayer of molecules with opposing dipole moment, but with equal molecule length, to minimize the effect of locally modifying the contact resistance at the injecting contacts, which might otherwise dominate the device performance. Since the extra resistance is based on charge carriers tunneling through the SAM, it will strongly depend on the thickness of the SAM. By using molecules with the same length, the influence of the SAM thickness on the observed differences in device current will be minimized, and those differences can be solely explained by the surface potential shift due to the dipole moment of a single layer of molecules.

Here, we present a method to locally modify the work function of gold electrodes by patterning different SAMs using microcontact printing. Utilizing this process, the anode of a polymeric light-emitting diode (PLED) is patterned, on a micrometer length scale, with SAMs possessing opposing dipole moments which consequently control the local charge injection and, therefore, the local light-emission of the PLED. Compared to photolithographically defined electrodes, this process is a simple and inexpensive method to pattern electrodes with a high resolution and potentially finds applications in static displays, for example in signage, labeling or packaging.

## 2 Experimental

Patterns of self-assembled monolayers (SAMs) on gold electrodes were created by transferring molecules (alkanethiols or perfluorinated alkanethiols) onto the gold surface using a poly(dimethylsiloxane) (PDMS) stamp. Glass substrates were first cleaned with detergent, acetone and 2-propanol. 1 nm chromium, as an adhesive layer, and a semitransparent layer of 10 nm gold were thermally evaporated through a shadow mask on the substrates. Elastomeric stamps were fabricated by pouring PDMS (Sylgard 184, Dow Corning) onto a pre-patterned silicon master and curing in an oven at 60°C for 2 h. The stamps were inked by soaking the stamp with a 3 mM ethanol solution of either 1-decanethiol (DT), 1-tetradecanethiol (TDT) or $1H,1H,2H,2H$-perfluorodecanethiol (PFDT). After typically 2 h, the stamps were blown dry in a flow of nitrogen, and brought in gentle contact with the gold electrodes for typically 30 s. After the stamping procedure, the samples were either rinsed with ethanol to create a substrate with Au and a patterned SAM, or immersed in a 3 mM ethanol solution with molecules with an opposing dipole moment for 20 s to create a larger contrast in work function by using two SAMs simultaneously on one electrode, and then rinsed with ethanol. Reference devices were fabricated using glass substrates with an anode of pre-patterned Indium Tin Oxide (ITO) and a 60 nm thick film of Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS).

As the semiconducting film, poly(2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylene vinylene) (MEH-PPV) was spin-coated from a toluene solution in a nitrogen environment. The devices were completed by depositing a top electrode by thermal evaporation of 5 nm barium and 100 nm aluminum.

Current–voltage characteristics were obtained in a nitrogen atmosphere, using a Keithley 2400 source meter unit, controlled by a PC with a LabVIEW program. Simultaneously, the light output was recorded by measuring the current from a photodiode connected to a Keithley 6514 Electrometer unit.

Samples for Kelvin probe measurements and scanning Kelvin probe microscopy (SKPM) were prepared by evaporating 1 nm chromium and 10 nm gold on glass and on a cleaned silicon wafer (with 500 nm silicon oxide), respectively, followed by patterning the SAM according to the procedure described above.

Kelvin probe measurements with a lateral resolution of a few millimeters were conducted with a Kelvin probe, calibrated with freshly cleaved highly oriented pyrolytic graphite (HOPG) under $N_2$. Freshly cleaved HOPG is known to have a stable work function of 4.48 eV [25].

SKPM measurements were performed using an AFM (Multimode SPM connected to a NanoScope IV, Veeco) with a conducting tip (platinum-coated ElectriTap300, purchased from Innovative Solutions Bulgaria Ltd.), with a resonance frequency of 300 kHz, force constant of 40 N/m and cantilever length of 125 μm. Each AFM tapping mode scan is followed by a scan where the tip is lifted typically 20 nm and a voltage is applied to the tip, to measure differences in local surface potential.

## 3 Results and discussion

To clearly visualize the concept of manipulating charge injection with a single layer of molecules and to present a real-life application, we fabricated patterned PLEDs based on patterns of SAMs. We patterned the SAMs by microcontact printing different thiol-based molecules onto gold substrates using a PDMS stamp and used this as the anode of a PLED.

The work function ($\Phi$) of gold modified with a SAM was determined using Kelvin probe measurements. The different molecules were applied to gold substrates using millimeter-sized PDMS stamps without a relief pattern, large enough for our Kelvin probe setup. For gold with a stamped DT SAM and a stamped PFDT SAM, we measured a work function of 4.3 eV and 5.5 eV, respectively, which is a shift of $-0.5$ eV and $+0.7$ eV with respect to bare, vapor-deposited gold.

To compare the light-emission from devices with different SAM-modified anodes, light-emitting diodes (LEDs) were fabricated [26]. The devices consist of a glass substrate with Au (with or without a SAM), MEH-PPV (165 nm) as the light-emitting polymer and a Ba (5 nm)/Al (100 nm) cathode for efficient electron injection under forward bias. To achieve optimal SAM quality, the SAMs in these devices were assembled from solution. As a reference, devices with an ITO/PEDOT:PSS (60 nm) anode were fabricated as well, with the same light-emitting layer and cathode. Current density ($J$) vs. voltage ($V$) plots are shown in Fig. 1(a), and the corresponding light-output of the devices is shown in Fig. 1(b). The graphs show a clear decrease in current density for the LED with a DT-modified anode, and a significant increase in current for the PFDT-modified LED, when compared to the device based on pristine gold. The same change is observed in the light-output of the devices. Furthermore, devices with a PFDT-modified gold electrode show a performance approaching that of devices with an ITO/PEDOT:PSS anode, which is the most widely used Ohmic anode for PLEDs based on PPV-derivatives.

The HOMO level of MEH-PPV is approximately 5.3 eV [20, 27]. Therefore, the LEDs based on vapor deposited gold ($\Phi = 4.8$ eV) demonstrate an injection limited hole current due to the mismatch of the HOMO level of MEH-PPV and the work function of gold. Modifying the effective work function of the gold anodes with a PFDT SAM creates an Ohmic contact, whereas gold modified with an alkanethiol results in an even larger injection barrier for holes, as was demonstrated before [20, 21]. Comparison of the two SAM-modified LEDs results in a vast ratio of 4 orders of magnitude in current density, as well as in light-output. Since the SAMs determine the work function shifts, the light-emission contrast depends on the quality of the SAMs. Since the quality of a SAM assembled from solution is generally better than of a printed SAM, we consider a factor of $10^4$ contrast difference in light-emission the upper limit achievable with printed SAMs in PLEDs based on PPV-derivatives. The modification of the light-output of a polymer LED simply by applying a SAM to one of its electrodes, is the effect we will exploit for patterned PLEDs.

Subsequently, as a proof of principle, we applied a DT-SAM to one corner of the gold anode of a millimeter-sized PLED, to locally block the hole injection and, consequently, the light-emission. Again, a PDMS stamp without a relief pattern was used, using the inking and stamping processes as described before. Thus, the PLED stack is as follows: Glass/Cr (1 nm)/Au (10 nm, with or with-

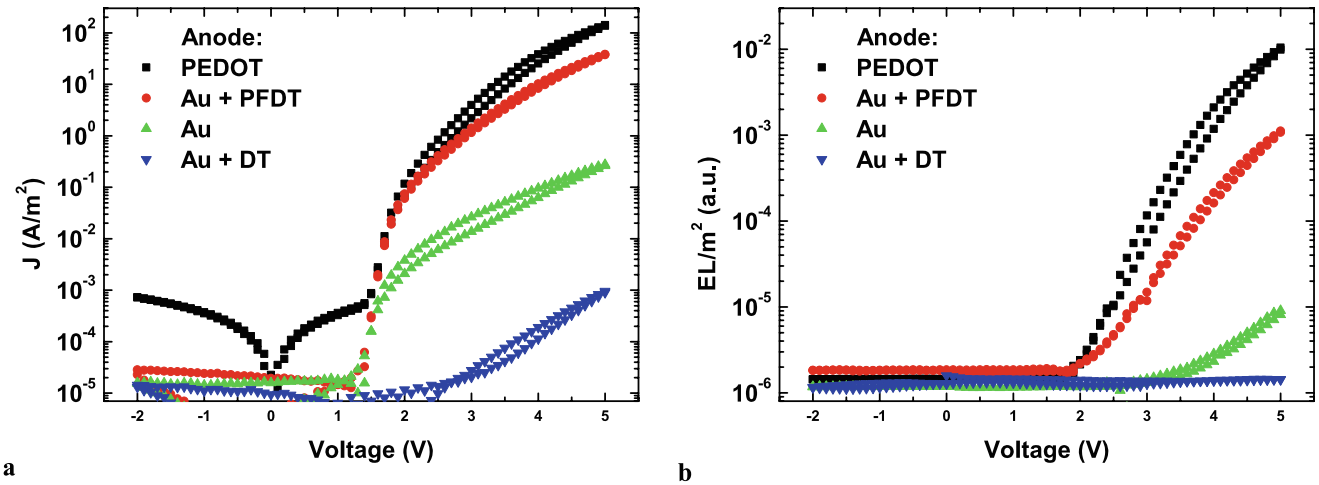



**Fig. 1** Comparison of light-emitting diodes (LEDs) with different anodes. All devices have an active area of 16 mm$^2$ and their structure is: Anode/MEH-PPV (165 nm)/Ba (5 nm)/Al (100 nm). **a** Current density versus applied voltage. **b** Electroluminescence versus applied voltage. A difference of 4 orders of magnitude in current-density and in light-output is observed, between devices with DT and PFDT modified Au anodes

out SAM)/MEH-PPV/Ba (5 nm)/Al (100 nm). As can be seen in Fig. 2(a), the emission of light from the stamped corner, where Au is modified with DT, is reduced significantly compared to the light-emission from the pristine Au. As demonstrated in Fig. 1, a moderate hole injection barrier is found for vapor-deposited Au anodes ($\Phi = 4.8$ eV). Therefore, to dramatically enhance the difference of the local work functions, the pristine Au ($\Phi = 4.8$ eV) was back-filled with the PFDT SAM ($\Phi = 5.5$ eV) from an ethanol solution to increase the contrast in light-emission due to the improved hole injection from these areas with the PFDT SAM, as shown in Fig. 2(b).

The macroscopic demonstration of patterning SAMs on the anodes of PLEDs, motivated us to explore the patterning of PLEDs with a much higher resolution using microcontact printing (μCP), which allows us to control the local light-emission on a micrometer length scale. The latter is considered a very simple and inexpensive method for high resolution static displays, which eliminates expensive processing steps such as photolithography to define the pixel area. Therefore, PDMS stamps with a relief pattern, fabricated by molding from a silicon master which was created by selectively etching the silicon, were used to apply micrometer-sized patterns of SAMs onto gold substrates. In order to relate light-emission to the local work function, scanning Kelvin probe microscopy (SKPM) measurements were performed on the micro-patterned SAMs to determine the local work function of the SAM-modified gold surface (Fig. 3). A SAM pattern with 1 μm wide lines and 1 μm spacing was applied to a gold surface and the local work function was recorded using SKPM. For a PFDT SAM, a work function shift of typically 70 meV was observed for the 1 μm periodic line sequence (Fig. 3), which is significantly smaller than the shift of +0.7 eV, observed for macroscopic PFDT-modified Au areas, as shown before. We attribute this smaller observed surface potential difference to the effect of non-local coupling between the entire AFM tip (cantilever) and the SAM surface, which is studied in detail by Charrier et al. [28].

The micro-patterned SAM on gold was used as the anode of a PLED, and the light-emission was recorded with an optical microscope. The structure and fabrication of the micro-patterned PLED are identical to those of the macro-

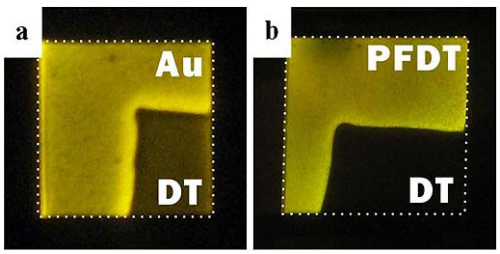



**Fig. 2** Images of polymer LEDs with a SAM-patterned Au anode: **a**, **b** Photographs of an PLED with an active area of 6 × 6 mm (**a**) and of 10 × 10 mm (**b**), with a DT-SAM patterned on the bottom-right corner. The *dashed white line* indicates the anode/cathode overlap region, i.e., the maximum emissive area. The LED in (**b**) is back-filled with a PFDT SAM from solution, for an enhanced contrast in light-emission

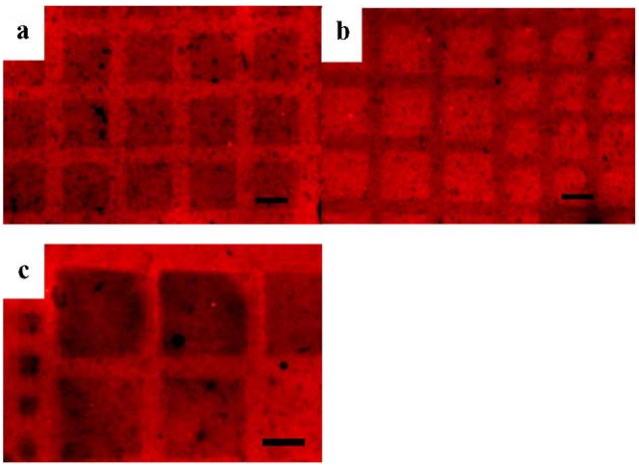
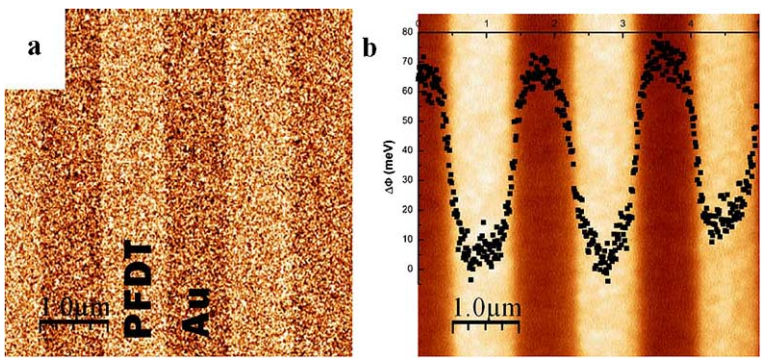



**Fig. 4** **a** Optical micrograph of a PLED with a patterned DT SAM (30 and 40 μm squares) operating at 6.6 V, **b** optical micrograph of a PLED with a patterned PFDT SAM (20 and 30 μm squares) operating at 7.3 V and (**c**) optical micrograph of a PLED with a microcontact printed DT SAM, where the unmodified Au was back-filled with a PFDT SAM from an ethanol solution for increased contrast in light intensity (10 and 40 μm squares), operating at 6.8 V. *Scale bars*: 20 μm

**Fig. 3** A SAM of microcontact printed PFDT on gold with a pattern of 1 μm wide lines, scan-size 5 × 5 μm; **a** the AFM height plot where the patterned SAM is visible, **b** the corresponding SKPM plot with a work function difference of about +70 meV between the PFDT SAM and gold



scopically patterned PLED, the difference being a SAM pattern with much smaller features. The stamp pattern consisted of repeating squares, ranging in size from 10 to 40 μm and a relief height of 20 μm. As shown in Fig. 4, regions with a DT SAM show a lower light intensity compared to the surrounding pristine gold, Fig. 4(a), and regions modified with microcontact printed PFDT demonstrate an increased intensity, Fig. 4(b). Thus both positive and negative tones can be created by selectively applying the correct SAM. By applying both SAMs simultaneously, thus stamping a pattern of DT and back-filling the pristine gold with PFDT by immersion in an ethanol solution, the contrast in light intensity can be enhanced substantially, as shown in Fig. 4(c).

## 4 Conclusion

We have demonstrated that by patterning a gold anode of a PLED with a single layer of thiolate molecules, with a thickness of ∼1.5 nm but with opposing dipole moments, the local light-emission of the device can be controlled. The molecules form a chemisorbed monolayer on the gold surface, thereby changing the work function of the metal locally. The work function of gold surfaces with a SAM of DT or PFDT, applied by microcontact printing, has been modified on two lateral length scales, resulting in a large modification of the local light-emission. Kelvin probe measurements on SAM-modified gold demonstrate a work function difference between gold modified with a DT and a PFDT of typically >1 eV. SKPM measurements on micrometer-sized features result in a much smaller contact potential difference for 1 μm line patterns of a SAM on Au, due to nonlocal coupling between the entire cantilever and the substrate.

Microcontact printed patterns of SAMs on gold have been used as the anode for PLEDs, in which the work function difference between SAMs with opposing dipole moment is utilized to control the hole injection, and consequently the light-emission. Since the hole injection from the anode to the electroluminescent polymer MEH-PPV depends strongly on the difference between the work function of the anode and the HOMO of the polymer, the contact can be tuned locally from Ohmic (Au modified with PFDT) to severely injection-limited (Au modified with DT). The optical result is a high contrast in light-emission, which can be used for several low-end applications such as static displays.

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